

Several simplifying assumptions have been made above, which warrant comments. First, it has been assumed that backward crack motion does not occur, even below $G = 2\gamma$. This could be rationalized in terms of local rearrangement of the atoms after bond breaking; due to the lack of long-range order in glass, it is not unreasonable to expect some local rearrangement after bond rupture [8]. Lateral relaxation of atoms across the fracture plane would make it more difficult to re-form broken bonds. Although there is evidence for crack healing in glass [8], no complete strength recovery has been observed. Secondly, γ_t has been assumed equal to γ , which implies rather severe lattice trapping; this would follow if the crack tip were very narrow, so that the crack tip stresses are essentially localized in one bond. Finally, the whole treatment rests on the assumption that crack motion in glasses occurs by the breaking of single bonds and the resulting increase of crack area by $\sim b^2$; by contrast, if the crack were perfectly straight and moved rigidly through the solid, for an amorphous material dU_s/dA would be independent of the position of the crack and no lattice trapping would be expected.

In summary, the present paper has shown that slow crack growth of glass in vacuum can be explained by the thermally activated breaking of bonds at the crack tip within the framework of the "lattice trapping" theory.

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References

1. A. A. GRIFFITH, *Phil. Trans. Roy. Soc.* **A221** (1920) 163.
2. J. B. WACHTMAN, JUN., *J. Amer. Ceram. Soc.* **57** (1974) 509.
3. W. B. HILLIG and R. J. CHARLES, "High Strength Materials", edited by V. F. Zachay, (John Wiley, New York, 1965) p.682.
4. B. R. LAWN, *J. Mater. Sci.* **10** (1975) 469.
5. S. M. WIEDERHORN, H. JOHNSON, A. M. DINESS and A. H. HEUER, *J. Amer. Ceram. Soc.* **57** (1974) 336.
6. S. M. WIEDERHORN *ibid* **52** (1969) 52.
7. W. D. KINGERY, "Introduction to Ceramics" (John Wiley, New York, 1960) p.148.
8. S. M. WIEDERHORN and P. R. TOWNSEND, *J. Amer. Ceram. Soc.* **53** (1970) 486.

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Comment on "Dielectric behaviour and morphology of poly(vinylidene fluoride)"

The recent paper by Baird *et al.* [1] presents some novel data on oriented poly(vinylidene fluoride) (PVDF) which is particularly interesting since measurements are made both parallel and perpendicular to the orientation direction. Whilst not questioning the validity of this data we would like to suggest a very different interpretation of the anisotropy observed.

The authors of this paper, in common with other investigators, suggest that the anisotropy of ϵ^{\parallel} at -20°C implies an oriented amorphous phase. Since the samples were drawn at 169°C and T_g is $\sim -40^{\circ}\text{C}$ this is extremely unlikely. We prefer to view the data as an extreme example of form

birefringence, that is, the anisotropy is a consequence of the shape and orientation of the crystallites rather than arising from an anisotropic amorphous phase.

A detailed analysis is prohibitive since it would require a knowledge of the lamellar shape factors and orientation functions which is not easily obtainable from low-angle X-ray data. In particular, the line-collimated low-angle X-ray data used by the authors do not easily yield data on the orientation of the lamellae. Similar samples studied by us, however, using a point-collimated low-angle apparatus yield a typical pattern consisting of two arcs of half angle $\sim 35^{\circ}$ indicating a concentration of lamellar normals along the draw direction. Measurements made perpendicular to the draw direction, therefore, tend to see the two phases

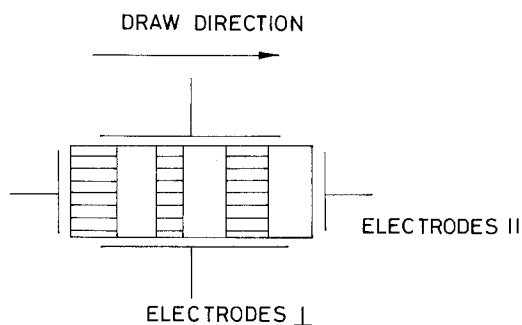


Figure 1 The relative orientation of lamellae and electrodes in the "parallel" and "perpendicular" configurations.

essentially in parallel, and along the draw direction in series (Fig. 1). If the crystallinity is χ we therefore expect, using an obvious notation

$$\epsilon_{\perp} = \chi \epsilon_{\perp}^c + (1 - \chi) \epsilon_{\perp}^a$$

$$\frac{1}{\epsilon_{\parallel}} = \chi \frac{1}{\epsilon_{\parallel}^c} + (1 - \chi) \frac{1}{\epsilon_{\parallel}^a}$$

It is our contention that $\epsilon_{\parallel}^a = \epsilon_{\perp}^a$, i.e. the amorphous phase is isotropic; therefore, the above two equations have three unknowns, ϵ_{\perp}^c , ϵ_{\parallel}^c and ϵ^a , and we cannot solve these without further approximation. Since the crystalline phase exhibits a dipolar process well above room temperature, we are essentially concerned with birefringence of the crystals below room temperature which is typically small; therefore, assume $\epsilon_{\perp}^c \approx \epsilon_{\parallel}^c$ below 20°C. Above 20°C, well above the β process, ϵ^a should be essentially constant, say at its value at 20°C. For simplicity let $\chi = 0.5$, then Equations 1 and 2 may be solved to give:

below 20°C

$$\epsilon^a = \epsilon_{\perp} \left\{ 1 + \left(1 - \frac{\epsilon_{\parallel}}{\epsilon_{\perp}} \right)^{1/2} \right\}$$

$$\epsilon^c = 2\epsilon_{\perp} - \epsilon^a,$$

above 20°C

$$\epsilon_{\perp}^c = 2\epsilon_{\perp} - \epsilon^a$$

$$\epsilon_{\parallel}^c = \left\{ \frac{2}{\epsilon_{\parallel}} - \frac{1}{\epsilon^a} \right\}^{-1}.$$

If these equations are applied to the data of Baird *et al.* they yield the result shown in Fig. 2. In view of the gross simplifications involved, the result is gratifying in that the step in ϵ^a is very large at -20°C compared with the step in ϵ^c

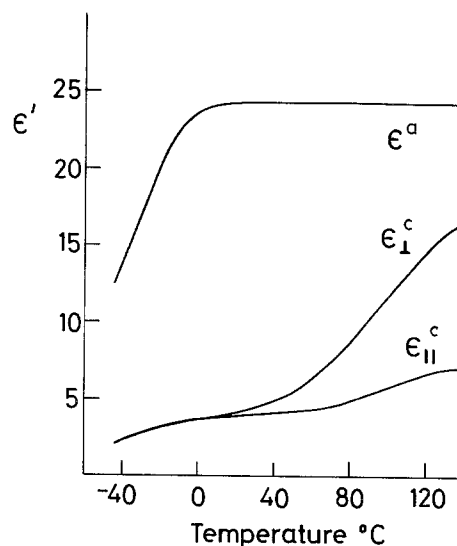


Figure 2 The amorphous and crystalline contributions to the permittivity calculated from the equations in the text and the data of [1].

which is relatively slowly varying in this region, and the pattern of anisotropy of ϵ^c is consistent with dipole rotation about the chain axes as suggested by Baird *et al.* Note, however, that the anisotropy of ϵ^c on this model is much greater than that indicated by the raw data without correction for the form effect.

To summarize, therefore, we believe that the orientation of the crystal lamellae has a profound effect upon the permittivity of PVDF since the lamellae are essentially thin plates and the disparity between the permittivities of the two phases is large. Although a detailed analysis is prohibitive, the naïve model presented here demonstrates the plausibility of the effect and shows how it can affect the analysis of both the amorphous (β) and crystalline (α) processes.

Reference

1. M. E. BAIRD, P. BLACKBURN and B. W. DELF, *J. Mater. Sci.* **10** (1975) 1248.

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Reply to 'Comment on "Dielectric behaviour and morphology on poly(vinylidene fluoride)"'

We are grateful for the comments by Davies and Rushworth [1] and their alternative explanation for the dielectric data on oriented polyvinylidene fluoride (PVDF) published previously [2]. These data were obtained from measurements on specimens parallel and perpendicular to the draw direction and also on isotropic specimens and showed a similar anisotropy for both the α (associated with crystalline regions) and β (associated with amorphous regions) relaxations.

The anisotropy of the α relaxation was interpreted in terms of chain motion within the lamellae [3], and the analysis of Davies and Rushworth supports this conclusion. The anisotropy of the β relaxation was suggested as being due to some "lining up" of the chains in the amorphous regions, but the analysis of Davies and Rushworth, on the basis of a two phase model with an isotropic amorphous phase, gives an alternative explanation.

The samples were drawn at 169° C and, with $T_g \approx -40^\circ$ C, Davies and Rushworth suggest an oriented amorphous phase is not likely. However, similar studies with polychlorotrifluoroethylene (PCTFE) of low crystallinity ($\approx 35\%$) drawn at $\approx 100^\circ$ C with $T_g \approx 50^\circ$ C also exhibit the same anisotropy for the β relaxation [4].

Considerable wide-angle and small angle (both point and slit collimated) X-ray work has been done by us on oriented and isotropic PVDF, but this was not included in the previous paper. However, a non-uniform amorphous halo is not visible in the oriented samples.

It is difficult to distinguish which explanation for the anisotropy of the β relaxation is correct, for this depends on whether or not there is a truly isotropic amorphous component. This problem has not been completely resolved yet, but there seems to be considerable evidence in support of a degree of ordered chain packing in so called amorphous regions (see, for example, [5]).

References

1. G. R. DAVIES and A. RUSHWORTH, *J. Mater. Sci.* **11** (1976) 782.
2. M. E. BAIRD, P. BLACKBURN and B. W. DELF, *ibid* **10** (1975) 1248.
3. M. E. BAIRD and P. BLACKBURN, *ibid* **7** (1972) 836.
4. *Idem*, *ibid* **9** (1974) 1099.
5. G. S. Y. YEH, *Polymer Preprints* **14** (1973) 718.

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Correlation between electric strengths and heats of atomization of gaseous dielectrics

In high-voltage technology, gaseous materials are frequently used as dielectrics and it is of central interest to delineate the fundamental factors which determine the relative electric strengths of various gases. For a given gas, the Paschen's law [1] describes quantitatively the breakdown strength in terms of the gas pressure, electrode separation and related physical parameters; this law does not permit, however, to correlate the breakdown strength of a gas with its basic physico-chemical characteristics. With the success of SF₆ as a gaseous dielectric in high-voltage technology, it was generally felt that the symmetrical bonding (and

thence the zero dipole moment) of SF₆ is probably responsible for its high electric strength. With the discovery of several fluoro compounds, especially the fluoronitriles (Table I), it became clear that symmetrical bonding and zero dipole moment are not the primary factors responsible for the high electric strength of gases. We have found that high electric strengths of gases are directly related to their heats of atomization per mole (Fig. 1) for gases for which the appropriate data are available in the literature (Table I). It would thus appear that the physico-chemical event responsible for the electric breakdown of a gas is the complete atomization of its molecules into the constituent atoms. In other words, high electric strengths are associated with gases for which high amounts of energy are